PATENT SPECIFICATION

NO DRAWINGS.

895,980

COMPLETE SPECIFICATION.

Block Polymers and Process for Production thereof.

We, PHILLIPS PETROLEUM COMPANY, a corporation organised under the laws of the State of Delaware, United States of America, of Bartlesville, Oklahoma, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement :—

This invention relates to the preparation of block polymers and more particularly to a process for preparing novel block polymers of certain conjugated dienes and other unsaturated materials.

It is known that various types of polymers can be prepared from different monomeric materials, the particular type formed being generally dependent upon the procedure followed in contacting the materials in the polymerization zone. For example, copolymers, such as a butadiene-styrene copolymer, can be prepared by the simultaneous reaction of the copolymerizable monomers. It is also possible to prepare polymers which are commonly known as graft polymers. Graft polymers result from the joining of a comonomer to an already formed polymer at random points along the polymer chain. Still another type of polymer can be obtained by following a procedure known as block polymerization. The polymers, usually referred to as block polymers, are formed by polymerizing a monomer on to the end of a polymer, the monomer being introduced in such a manner that substantially all of the co-reacting molecules enter the polymer chain at this point. The particular method used in preparing the polymers has a great influence upon the properties of the product obtained. Thus, copolymers, graft polymers and block polymers differ greatly in their properties even though the weight per cent of each of the monomeric materials contained in the polymer may be the same in each case.

One object of this invention is to provide a novel process for preparing block polymers of selected conjugated dienes and other unsaturated monomeric materials. Further, the block polymers of the present invention are characterized in that the molecules which form same have substantially the same molecular weight.

According to the present invention there is provided a process for preparing block polymers from monomers selected from (1) 1,3-butadiene, 2-methyl-1,3-butadiene, 1,3-pentadiene and vinyl-substituted aromatic hydrocarbons, (2) vinyl pyridines and (3) vinyl halides, vinylidene halides, acrylonitrile, esters of acrylic acid and esters of homologues of acrylic acid, which comprises initially contacting a first monomer selected from the monomers in said groups (1) and (2) with a catalyst corresponding to the formula $R(Li)_x$, wherein R is a hydrocarbon radical selected from aliphatic, cycloaliphatic and aromatic radicals and x is an integer from 1 to 4, inclusive, in the presence of a hydrocarbon diluent selected from aromatic, paraffinic and cyclo-paraffinic hydrocarbons so as to form a polymer block of said selected monomer ; and, after polymerization of substantially all of said selected first monomer, contacting said catalyst in the presence of said polymer block and said hydrocarbon diluent (A) with a second monomer selected from the monomers in said groups (1), (2) and (3) when said first monomer is a monomer of group (1) or (B) with a second monomer selected from the monomers in said group (3) when said first monomer is a monomer of group (2), said second monomer

being different from the monomer employed in said initial contacting.

The present invention also provides a block polymer of substantially uniform molecular weight prepared in the presence of a lithium-containing catalyst, which comprises at least two polymeric blocks linked to on another, one of said polymeric blocks being formed by the polymerization of at least one monomer selected from 1,3-butadiene, 2 - methyl - 1,3 - butadiene, 1,3-pentadiene, vinyl - substituted aromatic hydrocarbons, and vinylpyridines containing a vinyl radical as the sole substituent, and another of said polymeric blocks being formed by the polymerization of at least one monomer selected from 1,3-butadiene, 2-methyl-1,3-butadiene, 1,3-pentadiene, vinyl-substituted aromatic hydrocarbons, vinylpyridines containing a vinyl radical as the sole substituent, vinyl halides, vinylidene halides, acrylonitrile, esters of acrylic acid and esters of homologues of acrylic acid, said polymeric block formed by the polymerization of vinyl pyridines being linked only to a polymeric block formed by the polymerization of at least one monomer selected from vinyl halides, vinylidene halides, acrylonitrile, esters of acrylic acid and esters of homologues of acrylic acid, and at least one monomer used in forming said first-mentioned polymeric block being different from at least one monomer used in forming said second-mentioned polymeric block.

The invention resides in the discovery that block polymers of certain selected monomers can be prepared in the presence of an organo-lithium catalyst. The polymers prepared by the process of the present application are to be distinguished from copolymers in that the final polymeric product is made up of blocks or segments. According to a preferred embodiment the polymer product is made up of blocks, each of which is a homopolymer of one of the monomers employed in the process. However, it is to be understood that the block polymers of this invention can also include copolymer blocks and homopolymer blocks or only copolymer blocks.

It is important that the monomers be contacted with the organolithium catalyst in the above-described manner, for otherwise the block polymers of this invention are not formed. Thus, if a vinylpyridine from group (2) is used in the initial contacting, the second monomer must be one selected from among those included in group (3), i.e., a vinyl halide, a vinylidene halide, acrylonitrile, an ester of acrylic acid or an ester of a homologue of acrylic acid. However, when a monomer selected from group (1), i.e., 1,3-butadiene, 2-methyl-1,3-butadiene, 1,3-pentadiene or a vinyl-substituted aromatic hydrocarbon, is employed in the

initial contacting, the second monomer can be selected from groups (1), (2) or (3). It is to be noted that in no case is a monomer of group (3) utilized in the initial contacting step. In any of the above-described charging procedures, it is to be understood that mixtures of monomers selected from the described groups of materials can be used in preparing the block polymers of this invention. The invention, in general, results in the production of block polymers containing 2 or more individual polymer blocks, at least one monomer used in forming a polymer block being different from a monomer used in forming an adjacent polymer block.

While the invention is especially applicable to the production of polymers formed of homopolymer blocks, other different and non-equivalent polymer products can be obtained by following the procedures of other embodiments of the invention. Thus, in one embodiment, a conjugated diene, such as 1,3-butadiene, and a vinyl-substituted aromatic hydrocarbon, such as styrene, are charged simultaneously to a reaction zone containing a hydrocarbon diluent and the organolithium catalyst. The polymerization which occurs results in the formation of a homopolymer of the diene or a copolymer containing at the most a very small number of styrene units. After the polymerization has proceeded until, for example, 50 per cent of the diene has been converted, a polar organic compound, such as hereinafter described, is charged to the reaction zone. Because of the addition of the polar compound, a butadiene-styrene copolymer block is formed, thereby resulting in a block polymer product comprising a polybutadiene block and a butadiene-styrene copolymer block.

In another embodiment, a conjugated diene, such as 1,3-butadiene, is charged to a reaction zone containing a solvent mixture comprising a hydrocarbon and a polar organic compound and the organolithium catalyst. A portion of the butadiene, e.g. 25 per cent, is allowed to polymerize after which a second monomer, such as a vinyl-substituted aromatic hydrocarbon is added to the reaction zone. The resulting block polymer product comprises a homopolymer block of butadiene and a copolymer block of butadiene and the other monomer, e.g., styrene. In still another embodiment, a conjugated diene, such as 1,3-butadiene, and a vinyl-substituted aromatic hydrocarbon, such as styrene, are added to a reaction zone containing a solvent mixture comprising a hydrocarbon and a polar compound. The polymerization is allowed to proceed to 100 per cent conversion after which a conjugated diene is introduced to the reaction zone. The resulting block polymer product comprises a copolymer block and a homo-

polymer block. Alternatively, a mixture of monomers different from the first charge can be used as the second charge so as to give a block polymer product comprising copolymer blocks.

The organolithium compound used as a catalyst in the process of this invention corresponds to the formula $R(Li)_x$, wherein R is a hydrocarbon radical selected from aliphatic, cycloaliphatic and aromatic radicals and X is an integer from 1 to 4, inclusive. The R in the formula has a valence equal to the integer, and preferably contains from 1 to 20, inclusive, carbon atoms, although it is within the scope of the invention to use higher molecular weight compounds. Examples of these compounds include methyllithium, isopropyllithium, n - butyllithium, tert - octyllithium, n - decyllithium, phenyllithium, naphthyllithium, 4 - butylphenyllithium, p - tolyllithium, 4 - phenylbutyllithium, cyclohexyllithium, 4 - butylcyclohexyllithium, 4 - cyclohexylbutyllithium, dilithiomethane, 1,4 - dilithiobutane, 1,10- dilithiodecane, 1,20 - dilithioeicosane, 1,4- dilithiocyclohexane, 1,4 - dilithiobutene - 2, 1,8 - dilithio - 3 - decene, 1,4 - dilithiobenzene, 1,5 - dilithionaphthalene, 1,2 - dilithio- 1,2 - diphenylethane, 9,10 - dilithio - 9,10- dihydroanthracene, 1,2 - dilithio - 1,8 - diphenyloctane, 1,3,5 - trilithiopentane, 1,5,15- trilithioeicosane, 1,3,5 - trilithiocyclohexane, 1,2,5 - trilithionaphthalene, 1,3,5 - trilithio- anthracene, 1,3,5,8 - tetralithiodecane, 1,5,10,20 - tetralithioeicosane, 1,2,4,6 - tetra- lithiocyclohexane and 1,2,3,5-tetralithio-4- hexylanthracene.

Conjugated dienes which are used in preparing the block polymers of this invention are 1,3-butadiene, 2-methyl-1,3-butadiene (isoprene) and 1,3-pentadiene (piperylene). The vinyl-substituted aromatic hydrocarbons which can be employed in the practice of this invention can be any vinyl-substituted aromatic hydrocarbon. It is to be understood that a compound having a substituent on the alpha carbon atom, such as alpha-methylstyrene, is not applicable to the practice of the instant invention. Examples of vinyl-substituted aromatic hydrocarbons which can be advantageously utilized include styrene, 1-vinyl-naphthalene and 3-methyl-styrene.

The term " vinylpyridines " as used herein is intended to designate pyridines containing a vinyl radical as the sole substituent. The vinyl-pyridines which can be employed are 2-vinylpyridine, 3-vinylpyridine, and 4-vinyl-pyridine.

As heretofore indicated, vinyl halides and vinylidene halides can be used in the practice of this invention. Examples of suitable halides include vinyl chloride, vinyl bromide and vinylidene chloride. Esters of acrylic acid and esters of homologues of acrylic acid

can also be employed in preparing the block polymers of this invention. Examples of such compounds include methyl methacrylate, ethyl acrylate, ethyl ethacrylate, methyl acrylate, ethyl methacrylate, methyl propacrylate, propyl acrylate, n-butyl acrylate and phenyl methacrylate.

As mentioned hereinbefore, the polymerization is carried out in the presence of the diluent selected from the group consisting of aromatic, paraffinic and cyclo-paraffinic hydrocarbons. The preferred hydrocarbons of these types are those containing from 3 to 12, inclusive, carbon atoms. Examples of suitable hydrocarbons which can be used include propane, iso-butane, n-pentane, isooctane, n-dodecane, cyclopentane, cyclohexane, ethylcyclopentane, dimethylcyclopentane, methylcyclohexane, benzene, toluene, xylene, ethylbenzene and naphthalene. Mixtures of these various materials can also be employed. It is also within the scope of the invention to employ a polar compound, which does not inactivate the organolithium catalyst, in admixture with the hydrocarbon diluent. It has been found that the use of such polar organic compounds increases the rate at which the monomeric materials are polymerized. Examples of polar compounds which can be advantageously utilized are ethers, thio-ethers (sulfides) and tertiary amines. Specific examples of such polar materials include dimethyl ether, diethyl ether, ethyl methyl ether, ethyl propyl ether, di-n-propyl ether, di-n-octyl ether, anisole, dioxane, 1,2-di-methoxyethane, dibenzyl ether, diphenyl ether, tetramethylene oxide (tetrahydrofuran), dimethyl sulfide, diethyl sulfide, di-n-propyl sulfide, di-n-butyl sulfide, methyl ethyl sulfide, di-methylethylamine, tri-n-propylamine, tri-n-butylamine, trimethyl-amine, triethylamine, N,N-dimethylaniline, N-methyl-N-ethylaniline, N-methylmorpholine, pyridine and quinoline. It is to be understood also that mixtures of these polar compounds can be employed in the practice of the instant invention. The amount of polar compounds used in admixture with the hydrocarbon diluent is usually in the range of 0.005 to 50 weight per cent of the total mixture.

The polymerization process of this invention can be carried out at a temperature within the range of -80 to $150°$ C. However, it is preferred to carry out the process at a temperature in the range of -20 to $80°$ C. The polymerization reaction can be carried out under autogeneous pressures. It is usually desirable to operate at pressures sufficient to maintain the monomeric materials substantially in the liquid phase. The pressure will thus depend upon the particular materials being polymerized, the diluent being employed, and the tempera-

ture at which the polymerization is to be carried out. However, higher pressures can be employed if desired, these pressures being obtained by some such method as the pressurization of the reaction with a gas which is inert with respect to the polymerization reaction.

The amount of catalyst which is used in the preparation of the block polymers of this invention can vary over a rather wide range. In general, at least 0.3 milliequivalents, e.g., 0.3 to 100 milliequivalents, of the organolithium compound per 100 parts by weight of the total monomers to be polymerized is employed in the process. That is, with a monolithium initiator, at least 0.3 millimoles is used while with di-, tri-, or tetralithium initiators a corresponding smaller amount can be utilized, i.e., 0.15, 0.10 or 0.075 millimoles. The upper limit of the amount of the organolithium compound to be used depends primarily upon the desired inherent viscosity of the polymer resulting from the polymerization. The inherent viscosity of the polymer produced decreases with increasing amounts of the organolithium compound. A preferred catalyst level is from 0.6 to 15 milliequivalents of organolithium per 100 parts by weight of total monomers charged.

The polymerization process of this invention is conducted by initially charging the catalyst components and diluent to a suitable pressure-type reaction zone. The selected monomer (or monomers) to be initially polymerized is then charged to the reaction zone. The polymerization is allowed to proceed until substantially all of this monomer has been polymerized as indicated, for example, by the reduction in pressure which takes place in the reaction zone. After completion of the polymerization of the initial monomer charge, the reaction zone si repressured with another monomer which is different from the monomer originally charged, and the polymerization is again permitted to proceed until substantially all of this latter monomeric material has been polymerized. This procedure can then be repeated with alternating charges of different monomers until a block polymer of desired composition is obtained. It is necessary either to use up substantially all of each monomer charged before charging another or to remove unpolymerized monomer before the addition of another. Thus, it is to be understood that it is within the scope of the invention to allow the polymerization to proceed until a portion only of one of the monomer charges has been used up after which the remainder of this monomer is removed from the reaction zone. Another monomer is then added to the catalyst and polymer in the reaction zone. When using a conjugated diene as the initial monomer

charge, it is usually preferred to employ a monomer other than a conjugated diene as the second charge material. However, a conjugated diene different from the one initially charged can be used as the second charge.

Various materials are known to inactivate the catalyst composition of the invention. These materials include water, mercaptans, and primary and secondary amines. It is highly desirable, therefore, that the monomers be free of these materials as well as other materials which tend to inactivate the catalyst. Any of the known means for removing such contaminants can be used. Also, it is preferred that the diluent used in the process be substantially free of impurities such as water, oxygen and the like. In this connection, it is desirable to remove air and moisture from the reaction vessel in which the polymerization is carried out. Although it is preferred to carry out the polymerization under anhydrous or substantially anhydrous conditions, it is to be understood that some water can be tolerated in the reaction mixture. However, the amount of water which may be tolerated in the mixture is insufficient to completely inactivate the catalyst.

After the completion of the polymerization reaction, or after the polymerization has been carried out to the desired degree, the total reaction mixture is then treated to inactivate the catalyst and recover the polymer product. While it is to be understood that any suitable treating method can be employed, one method for accomplishing the desired treatment comprises adding a catalyst-inactivating material such as water, an alcohol, e.g., ethyl alcohol or isopropyl alcohol, an organic or inorganic acid. It is generally preferred to add only an amount of the catalyst-inactivating material which is sufficient to deactivate the catalyst without causing precipitation of the dissolved polymer. It has also been found to be advantageous to add an antioxidant, such as phenyl-beta-naphthylamine, to the polymer solution prior to precipitation of the polymer. After addition of the catalyst-inactivating material and the antioxidant, the polymer present in the solution can then be precipitated by the addition of an excess of a material such as ethyl alcohol or isopropyl alcohol. It is to be understood that deactivation of the catalyst and precipitation of the polymer can be accomplished in a single step. The precipitated polymer can then be recovered by filtration, decantation, or the like. In order to further purify the polymer, the separated polymer can be redissolved in a suitable solvent and again precipitated by the addition of an alcohol. Thereafter, the polymer is again recovered by a suitable separation means, as indicated hereinbefore, and dried. Any suitable hydro-

carbon solvent such as hereinbefore mentioned can be used in this purification step to redissolve the polymer. The diluent and alcohol can in all cases be separated, for example, by fractional distillation, and reused in the process. As hereinbefore mentioned, it is within the scope of the invention to utilize an antioxidant in the process to prevent oxidation of the polymer. The antioxidant can be added to the reaction mixture prior to precipitation of the polymer, to the solution of redissolved polymer, or to the diluent in which the polymer is to be subsequently redissolved.

A more comprehensive understanding of the invention can be obtained by referring to the following illustrative examples which are not intended, however, to be unduly limitative of the invention.

EXAMPLE I.

A series of runs was made in which butadiene-styrene block polymers were prepared by the process of this invention.

The n-butyllithium solutions used in these runs were prepared in the following manner. A 1000 milliliter, three-necked flask, fitted with a reflux condenser, a dropping funnel with a gas outlet sidearm, and a high speed stirrer, was swept with prepurified nitrogen and charged with 200 milliliters of dry, olefin-free petroleum ether and 3.8 grams of lithium wire which was cut into lengths of about 0.5 centimeter. The dropping funnel was then attached, and a solution of 23 grams of 1-chlorobutane in 100 milliliters of petroleum ether was charged to the dropping funnel. The stirrer was then started and brought to high speed after which the chlorobutane solution was added without cooling at a rate so as to maintain gentle reflux. When the addition of the chloro-

butane solution was completed, stirring was continued for 1 to 2 hours, after which the mixture was allowed to stand overnight. The contents of the flask were then transferred to a container by a suitable suction arrangement through ¼″ stainless steel tubing. The container was then centrifuged and the supernatent n-butyllithium solution was carefully pressured into a dry, nitrogen-filled bottle. Analysis showed that the solution was about 0.462 molar with respect to n-butyllithium.

The polymerization runs described herein were conducted in 7 and 12-ounce beverage bottles which were first charged with the appropriate amount of dried reaction solvent. Prepurified nitrogen was dispersed through a fritted glass tube and bubbled through the solvent at the rate of 3 liters per minute for 3 to 20 minutes. For 10 to 20 grams monomer charges, the bottles were first capped with rubber gaskets and metal caps, and the monomer and alkyllithium were introduced in that order by means of a syringe. Large monomer charges were weighed in before capping. The charged bottles were then agitated in constant temperature baths for the required polymerization time.

To terminate polymerization, 50 to 100 milliliters of a benzene or toluene solution containing about 5 per cent by weight isopropyl alcohol and 2 per cent by weight phenyl-beta-naphthylamine was added. The amine was added to serve as an antioxidant. The rubbery polymer was then precipitated by adding an excess of isopropyl alcohol after which the polymer was dried in a vacuum oven.

The following polymerization recipe was employed in these runs.

	Parts by Weight
1,3-Butadiene	75 or 100
Styrene	25 or 100
Cyclohexane*	390
n-Butyllithium**	0.16 (2.5 Millimoles)
Temperature, °C.	50
Time, hours	3 or 6

* The cyclohexane prior to use was bubbled with prepurified nitrogen for 30 minutes at 3 liters/minute and again for 5 minutes at this rate after charging to the bottle.

** An 0.462 molar solution of n-butyllithium in pentane was employed.

In these runs, the cyclohexane was always charged first, while the other materials were charged in several different orders. In this and in subsequent examples, when preparing the block polymers of this invention, an individual monomer charge was polymerized substantially to completion before the addition of another monomer charge. The

results of these runs are set forth hereinbelow in Table I. In Table I, the abbreviations Bd, Sty and BL designate, respectively, 1,3-butadiene, styrene and butyllithium. The times shown in the table indicate as applicable the interval between charges or the period from the last charge until the polymerization was terminated.

TABLE I.

Run Number		Total Reaction Time, Hours	Conversion %
1	Bd & BL—3 hours—Sty—3 hours	6	100
2	½ Bd & BL—2 hours—Sty—2 hours—½ Bd— 2 hours	6	92
3 (control)	Bd & BL—6 hours	6	72
4 (control)	Bd & BL—3 hours	3	70
5 (control)	Sty & BL—6 hours	6	100
6 (control)	Sty & BL—3 hours	3	100

* In this and subsequent examples, indicates per cent of total monomers converted to polymer.

The properties of the above prepared polymers are given below in Table II.

TABLE II.

Polymer from Run Number	Polymer Appearance	Refractive Index at 25° C. [1]	Inherent Viscosity	Styrene [2] Content Wt. %
1	Rubbery	1.537	0.88	24—26
2	Rubbery	1.5350	0.97	23.2
3	Soft, clear	1.5182	1.08	0
4	Soft, clear	—	—	0
5	White solid	—	0.34	—
6	White solid	—	—	—

[1] The refractive index determinations in this and succeeding examples were made on samples containing no antioxidant.
[3] As determined from a graph of refractive index versus styrene content.
NOTE : Dashes in this and subsequent tables indicate that the property was not determined.

Runs 1 and 2, which were carried out according to this invention, produced rubbery products.

In the above runs, none of the polymers contained gel.

EXAMPLE II.

Another series of runs was made following the procedure of Example I. The charge order in these runs was varied except for the solvent which was always charged first. These runs were conducted according to the following recipe.

RECIPE.

	Parts by Weight
1,3-Butadiene	75
Styrene	25
Cyclohexane*	390
n-Butyllithium*	0.16 (2.5 millimoles)
Temperature, °C.	50
Time, hours	6 hours

* See notes to recipe of Example I.

The results of these runs are given below in Table III. The abbreviations used in Table III are the same as those employed in Example I.

TABLE III.

Run Number	Charging Order and Procedure	Conversion %
7	Bd & Bl—3 hours—Sty—3 hours	} 99
8	Bd & BL—3 hours—Sty—3 hours	
9	½ Bd & BL—2 hours—Sty—2 hours—½ BD—2 hours	} 97
10	½ Bd & BL—2 hours—Sty—2 hours—½ BD—2 hours	—

Physical properties of the above polymers are shown below in Table IV. It is noted that the polymer products of each set of runs which were carried out under identical procedures were combined and the properties of the combined product measured.

TABLE IV.

Polymer from Runs Number	Inherent Viscosity	Refractive Index + 25° C. (1)	Styrene Content, Wt. %
7 & 8	0.85	1.5360	24.6
9 & 10	0.92	1.5362	25.0

(1) See note under Table II.

The polymers from runs 7 and 8, and 9 and 10, were then fractionated by solvent extraction to determine if homogeneous polymers were produced. As used herein, the term "homogeneous polymer" denotes a polymer in which fractions of different molecular weights have substantially the same average bound styrene content.

The procedure followed was to dissolve about 20 grams of the polymer to be analyzed for homogeneity in approximately one and one-half liters of toluene. A finite amount of methyl alcohol was then added so as to cause the precipitation of a portion of the dissolved polymer. After standing for about 24 hours, the precipitated phase was withdrawn and the polymer was recovered from this phase by stripping off the toluene over a hot water bath. The polymer was then dried in a vacuum oven. Each fraction was precipitated and recovered in this manner and then analyzed. The results are set forth in Table V.

The polymers so prepared were also subjected to an oxidation procedure which destroyed the polymer molecules containing unsaturation (polybutadiene). This oxidation method is based upon the principal that polymer molecules containing ethylenic bonds when dissolved in p-dichlorobenzene and toluene can be broken into fragments by reaction with tert-butyl hydroperoxide catalyzed with osmium tetroxide. Saturated polymer molecules or molecular fragments such as polystyrene or the polystyrene units in block polymers containing no ethylenic bonds remain unattacked. The small fragments (low molecular weight aldehydes) and the low molecular weight polystyrene fragments from the copolymer block are soluble in ethanol whereas the unattacked high molecular weight polystyrene from the styrene homopolymer block is insoluble in ethanol. It is thus possible to effect a separation of the high molecular weight polystyrene which constitutes the homopolymer block of the block polymer.

Approximately 0.5 gram of the polymer to be subjected to the oxidation procedure was cut into small pieces, weighed to within one milligram, and charged to a 125 ml. flask. Forty to fifty grams of p-dichlorobenzene was then charged to the flask, and the flask contents were heated to 130° C. The flask was maintained at this temperature until the polymer present had become dissolved. The solution was then cooled to 80 to 90° C., and 8.4 ml. of a 73.3 per cent by weight aqueous solution of tert-butyl hydroperoxide was added. One milliliter of 0.003 molar osmium tetroxide in toluene was then added to the flask contents, and the resulting solution was heated to between 110 and 115° C. for 10 minutes. The solution was then cooled to between 50 and 60° C., after which 20 ml. of toluene was added and the solution was poured slowly into 250 ml. of ethanol containing a few drops of concentrated sulfuric acid. Polystyrene coagulated out of solution and this polymer was recovered and dried. The amount of polystyrene recovered in this manner is shown in the last column of Table V. It is noted that in the case of runs 7—8 and 9—10, 22.6 and 21.8 weight per cent of polystyrene were recovered. Refractive index measurements of the same polymers showed 24.6 and 25.0 weight per cent styrene incorporation. It is thus seen that the oxidative degradation procedure does

not recover all of the available polystyrene. The difference in styrene analysis by refractive index and oxidation degradation has been found to be about 3 weight per cent in the case of this particular block polymer.

These data indicate that the products from run 7—8 and 9—10 were block polymers formed of homopolymer blocks of 1,3-butadiene and styrene.

TABLE V.

Polymer From Runs Number	Fraction	Weight % of Original	Inherent Viscosity	Refractive Index at 25° C. (1)	Styrene Content Weight %	Polystyrene Recovered by Oxidative Degradation, Wt. %
7 & 8	Original	100	0.85	1.5360	24.6	22.6
	1	46	0.97	1.5355	24.0	Not measured
	2	38	0.85	1.5369	25.5	Not measured
9 & 10	Original	100	0.92	1.5362	25.0	21.8
	1	42	0.94	1.5369	25.5	Not measured
	2	48	0.88	1.5379	27.0	Not measured
	3	10	0.49	—	—	Not measured

(1)   See note under Table II.

The values in Table V show that the block polymers prepared according to this invention were homogeneous polymers, i.e., the styrene content of the fractions is approximately the same as that of the total polymer.

EXAMPLE III.

A series of runs was conducted in which block polymers of 1,3-butadiene and acrylonitrile were prepared by a butyllithium-catalyzed polymerization. The butyllithium used in these runs was prepared as described in Example I, and the polymerization runs were carried out in beverage bottles as previously described. The polymerization recipes used are as follows.

RECIPES.

	Parts by Weight		
	A	B	C
Butadiene	0	50—100	75—50
Acrylonitrile	100	100—50	25—50
Cyclohexane a	390	390	390
n-Butyllithium b	Variable	Variable	Variable
Temperature, ° C.	50	50	50
Time, hours	21.5	21.5	21.5

a   Bubbled with prepurified nitrogen for 30 minutes in a one-gallon stock bottle and again in each 7 oz. beverage bottle for 5 minutes, using a nitrogen rate of 3 liters per minute.

b   0.252 M in pentane.

C   The butadiene was charged to the bottle in these runs and polymerization was initiated. After 3 hours reaction time, the acrylonitrile was charged. In recipes A and B, all of the monomer to be used was charged at the beginning of the run.

The results of these runs are set forth below in Table VI.

TABLE VI.

Run No.	Recipe	Butyllithium		Buta-diene parts	Acrylo-nitrile parts	Appearance		Conver-sion, %	Appearance of Product
		Milli-moles	Ml of 0.252 M soln			Upon Initiation	After Initiation		
11	A	15	5.95	0	100	Immediate yellow precipitate	Yellow ppt.	21	Yellow Powder
12	A	10	4.0	0	100	Immediate yellow ppt.	Yellow ppt.	14	Yellow Powder
13	A	5	2.0	0	100	Immediate yellow ppt.	Yellow ppt.	7	Yellow Powder
14	B	10	4.0	90	10	Immediate ivory ppt.	Ivory ppt.	9	Yellow Powder
15	B	10	4.0	75	25	Immediate yellow ppt.	Yellow ppt.	14	Yellow Powder
16	B	10	4.0	50	50	Immediate yellow ppt.	Yellow ppt.	14	Yellow Powder
17	B	5	2.0	75	25	Immediate yellow ppt.	Yellow ppt.	5	Yellow Powder
18	B	5	2.0	50	50	Immediate yellow ppt.	Yellow ppt.	6	Yellow Powder
19	C	10	4.0	75	25	Yellow soln.	Yellow soln.	91	Red, rubbery
20	C	10	4.0	50	50	Yellow soln.	Yellow soln.	32	Red, rubbery
21	C	5	2.0	75	25	Yellow soln.	Yellow soln.	78	Orange, rubbery
22	C	5	2.0	50	50	Yellow soln.	Yellow soln.	43	Orange, rubbery

In the above runs, it can be seen that the charging of butadiene and acrylonitrile at the beginning of the run (Recipe B) resulted in the immediate precipitation of a polymer similar to an acrylonitrile homopolymer (Recipe A). It can also be seen from the runs using Recipe C that block polymers result when butadiene is charged initially followed by the acrylonitrile.

The polymers prepared in the runs employing Recipe C were evaluated for certain properties. The results of these runs are given below in Table VII.

TABLE VII.

Polymer From Run No.	Refractive Index at 25° C.	Nitrogen Content, Wt. %	Acrylonitrile Wt. % (approx.)	Inherent Viscosity	Gel. %
19	1.5210	4.8	18	0.49	9*
20	1.5218	—	not calc.	0.23	0
21	1.5190	1.8	7	0.71	0
22	1.5188	—	not calc.	0.58	0

* Swelling Index = 20.

EXAMPLE IV.

A series of runs was carried out in which block polymers of 1,3-butadiene and 2-vinylpyridine were prepared by the intermittent charging procedure of this invention.

The butyllithium employed in these runs, which was prepared in the same manner as described in Example I, was charged in each of the polymerization runs as an 0.310 molar solution in cyclohexane. The polymerization recipes for these runs were as follows.

POLYMERIZATION RECIPES.

Ingredient	Parts by weight except as noted.			
	A	B	C	D
1,3-Butadiene	50	75	85	95
2-Vinylpyridine	50	25	15	5
Cyclohexane	780	780	780	780
n-Butyllithium	4 millimoles*	4 millimoles*	4 millimoles*	4 millimoles*
Temperature, ° C.	50	50	50	50
Total time, hours	5.5	5.5	5.5	5.5

* Millimoles per 100 parts of monomers.

In each of the runs employing the above recipes, the proper amount of cyclohexane was charged to a polymerization bottle after which the appropriate amount of butadiene was added. Polymerization was then initiated by charging the butyllithium. The butadiene polymerization was carried out for 4.5 hours, at which time the 2-vinylpyridine was introduced into each of the bottles. After one hour, polymerization was terminated by adding 16 parts by weight of isopropyl alcohol per 100 parts by weight of total monomer. The addition of this material caused precipitation of the polymer. Conversions were then determined by evaporating the solvent from the coagulated polymer.

The results of these runs are given below in Table VIII.

TABLE VIII.

Run No.	Recipe	Conversion %	Refractive Index at 25° C	Weight % vinylpyridine in polymer
23	A	98	—	—
24	B	100	1.5333	24.9
25	C	98	1.5267	15
26	D	96	1.5210	4.9

EXAMPLE V.

A series of runs was carried out in which isoprene-styrene block polymers were prepared according to the procedure of the foregoing examples. The polymerization recipes for these runs are given below.

RECIPE.

	Parts			
	A	B	C	D
Isoprene (MBd)	75	75	75	75
Styrene (S)	25	25	25	25
Cyclohexane	390	390	390	390
Ethyl ether	None	25	None	25
n-Butyllithium (BL) ..	Variable	0.26	Variable	0.26
Temperature, °F.	122	122	122	122
Time, hours (total) ..	8	8	8	8
Charge order	As shown in Table IX.			
Time between increments	4.0	4.0	2.67	2.67

The results of the runs which were made according to these recipes are expressed below as Table IX.

TABLE IX.

Run No.	Recipe	Butyllithium d PHM	MHM	Monomer Chg. Order a	Increment, Parts Isoprene	Styrene	Conversion %	Inherent Viscosity	Refractive Index @ 25° C.	Styrene Con. %b	Polystyrene Recovered by Oxidation Degradation Wt. %c	Inherent Viscosity
27	A	0.26	4.0	MBd-S	75	25	102	0.53	1.5361	24.5	21.7	0.15
28	A	0.19	3.0	MBd-S	75	25	103	0.91	1.5353	23.0	—	—
29	C	0.26	4.0	MBd-S-MBd	37.5	25	103	0.55	1.5354	23.5	20.7	0.14
30	C	0.19	3.0	MBd-S-MBd	37.5	25	103	0.78	1.5359	24.0	—	—
31	B	0.26	4.0	MBd-S	75	25	103	0.51	1.5328	22.0	21.9	0.12
32	D	0.26	4.0	MBd-S-MBd	37.5	25	101	0.72	1.5327	21.5	21.5	0.18

a   Total charge order was cyclohexane-ethyl ether-monomer increment-butyllithium-monomer increments.

b   As determined from a graph of refractive index versus styrene content.

c   As described in Example II.

d   PHM—Parts per hundred parts of monomer.
MHM—Millimoles per hundred parts of monomer.

e   Values above 100% because of slight overcharge of isoprene.

The polymer from run 29 was extracted to determine its homogeneity, the procedure described in Example II being followed. These extraction data are set forth below in Table X.

TABLE X.

Fraction	Weight %	Inherent Viscosity	Refractive Index @ 25° C.	Styrene Content, Wt.%
Original	100	0.59	1.5364	25.0
I	41.5	0.69	1.5330	20.0
II	8.8	0.57	1.5337	21.0
III	9.6	0.50	1.5348	22.5
IV	7.5	0.52	1.5350	23.0
V	10.5	0.46	1.5362	24.5
VI	14.0	0.45	1.5382	27.5
VII	1.9	0.19	—	—
Loss	6.2			

When proceeding in accordance with this invention, as in run 29, the data show that a homogeneous polymer is recovered as the product.

EXAMPLE VI.

A run was carried out in which a block polymer of butadiene and styrene was prepared by the intermittent charging procedure of this invention. The butyllithium was prepared in the same manner described in Example I. The proper amount of cyclohexane and diethyl ether was charged to the vessel after which the butadiene was added. Polymerization was then initiated by adding the butyllithium. The butadiene polymerization was carried out for 3 hours, at which time the styrene was introduced. After a period of 14 hours, the polymerization was terminated by the addition of an alcohol which caused the precipitation of the polymer. The polymerization recipe used in this run was as follows.

	Parts by Weight
Butadiene	75
Styrene	25
Cyclohexane	390
Diethyl ether	25
n-Butyllithium	0.19 (3.0 millimoles)
Temperature, ° F.	122 (50° C.)
Time, hours	17 (total)

The results of this run are set forth below in Table XI.

TABLE XI.

Conversion, per cent	100
Mooney viscosity, ML-4	38
Inherent Viscosity	1.09
Refractive Index at 25° C.	1.5319
Bound Styrene, per cent	21.0
Unsaturation by infra-red analysis, %	
Cis	20
Trans	30
Vinyl	27

The block polymer prepared as described above and a sample of a butadiene-styrene copolymer prepared by a typical emulsion polymerization were converted into compounded rubber stocks according to the following recipes.

Compounding Recipes.

	Parts by Weight	
	Block Polymer	Butadiene-Styrene Copolymer (3)
	A	B
Polymer	100	100
High Abrasion Furnace Black ..	50	50
Zince Oxide	3	3
Stearic Acid	1	1
Antioxidant (1)	1	1
Aromatic Oil (Plasticizer) ..	10	10
Sulfur -.. .. . =-	1.75	1.75
Vulcanization Accelerator (2) ..	1.2	1.2

(1) Physical mixture containing 65 per cent of a complex diarylamine-ketone reaction product and 35 per cent of N,N¹-diphenyl-p-phenylenediamine.

(2) N-cyclohexyl-2-benzothiazylsulfenamide.

(3) Butadiene-styrene copolymer prepared by emulsion polymerization at approximately 41° F., using a rosin acid soap emulsifier and a ferrous sulfate-sodium formaldehyde sulfoxylate activator and containing about 23.5 weight per cent bound styrene.

Physical properties of the raw compounded stocks and of the compounded stocks cured at 307° F. for 30 minutes and oven aged for 25 hours at 212° F. were determined. These properties are set forth hereinbelow in Table XII.

TABLE XII.

Recipe	Raw Compounded Stocks		30 min. Cure at 307° F.		Oven Aged 24 Hrs. at 212° F.	
	A	B	A	B	A	B
Mooney Viscosity (1)						
ML-4	38	52				
MS 1½ at 212° F.	43	36				
Scorch at 280° F. (2)						
Minimum ML-4..	34	37				
5 point rise minutes	16.8	26				
Extrusion at 250° F. (3)						
in./min.	85.0	43.5				
g./min.	122.0	110				
g./in.	1.44	2.35				
Rating	12	11				
$v \times 10^4$ moles/c.c. (4)			1.47	1.52		
Compression set, per cent (5)			19.7	20.9		
300% Modulus, p.s.i. (6)			2500	1425		
Tensile, p.s.i. (6)			2775	3685	2350	3500
Elongation, per cent (6)			330	555	210	390
200° F. Maximum tensile, p.s.i. (6)			1085	1840		
Hysteresis, T, °F. (7)			93.1	67.6	88.0	54.7
Resilience, per cent (7)			53.6	69.5	56.1	64.6
Flex Life, M (7) ..			4.6	31.4	1.3	3.3
Shore A Hardness (8)						
80° F.			81	60	84.5	66
212° F.			70	55.5	75	63.5
NBS Abrasion, rev./mil.. (9)			12.42	9.09		

(1) ASTM D-927-55T.

(2) Scorch is determined on a Mooney viscometer at 280° F. using the large rotor (ML-4). The scorch time is the time required for the Mooney value to rise a given amount above the minimum. The procedure is essentially the same as described by Shearer et al, India Rubber World *117*, 216–9 (1947).

(3) Extrusion is carried out at 250° F. by essentially the same procedure as described by Garvey et al, Ind & Eng. Chem. *34*, 1309 (1942). As regards the " rating " figure, 12 designates an extruded product considered to be perfectly formed whereas lower numerals indicates less perfect products.

(4) Determined by the swelling method of Kraus as given in Rubber World, October, 1946. This value is the number of effective network chains per unit volume of rubber. The higher the number, the more the rubber is crosslinked (vulcanized).

(5) ASTM 395–55.

(6) ASTM D412–51T.

(7) ASTM D623–55T.

(8) ASTM D676–55T.

(9) ASTM D394–47 (Method B). (NBS=National Bureau of Standards).

Examination of the data shown in Table XII indicates that the block polymer of this invention and the butadiene-styrene copolymer prepared by emulsion polymerization have different physical properties although they contain about the same amount of bound styrene. The high extrudability of the block polymer of this invention is one of its important properties since this property renders the polymer particularly suitable for certain uses, such as wire coating. The high extrudability can be attributed to the styrene block on the end of the polymer chains, which acts as a thermoplastic plasticizer for the polymer. The block polymer was thermoplastic and showed no shrinkage when molded. These properties render the block polymer especially suitable for use in

preparing molded articles. It is also seen from the data in Table XII that the block polymer stock exhibited a greater hardness and a greater resistance to abrasion than the butadiene-styrene copolymer stock.

EXAMPLE VII.

A run was carried out in which a block polymer was prepared by charging. to a polymerization bottle, as the initial charge, the following recipe.

	Parts by Weight
Butadiene	100
Cyclohexane a	780
Dilithiostilbene b c (millimoles)	3.34

a Dried over alumina, then by countercurrent nitrogen flow.
b 0.175 molar in ether and tetrahydrofuran.
c 1,2-dilithio-1,2-diphenylethane.

The cyclohexane solvent was charged to a polymerization bottle, and bubbled with dry nitrogen at the rate of 3 liters per minute for five minutes after which the butadiene was introduced and the catalyst added. Polymerization was allowed to proceed at 50° C. for 2 hours. At this point, a sample (Sample A, 48.3 gm.) was removed and treated with alcohol to inactivate the catalyst. To the bottle there was then added 25 grams of styrene. Polymerization was continued for an additional two hours at 50° C., after which alcohol was added to inactivate the catalyst.

The solution of Sample A which weighed 48.3 grams represented 23.9 per cent of the original charge and, calculated on the basis of butadiene in the charge, should at 100 per cent conversion yield 5.4 grams of polymer. On coagulation and recovery of the polymer, 5.4 grams was obtained. Thus, the original polymerization was quantitative. A similar calculation made on the styrene charge indicated that at quantitative conversion, 22.6 grams of block polymer should be obtained. Coagulation and recovery of the polymer yielded 23.2 grams or slightly more than theoretical, probably a result of a small overcharge of styrene.

Inherent viscosity was measured on the polymer from Sample A (polybutadiene) and on the block polymer. Values were as follows :

Inherent viscosity Sample A
 polymer 0.75
Inherent viscosity block polymer 0.84

Gel content and swelling index for both polymers were zero.

The foregoing run demonstrates that in both steps of the polymerization, 100 per cent conversion was obtained.

Two more runs were made using the same recipe, charging procedure, and polymerization time. At the end of the initial polymerization, 33.3 parts of styrene was added to one bottle, and the polymerization in the other bottle was stopped with alcohol. Polymerization was continued in the bottle to which styrene was added for an additional two hours at 50° C. after which the polymerization was stopped with alcohol. Both polymers were coagulated and recovered. Inherent viscosity of the polybutadiene was 0.79 and that of the block polymer was 0.82. It is to be noted that these values are essentially identical. Gel content and swelling index were zero.

The polybutadiene was a highly viscous liquid and physical properties were not determined. Evaluation of the block polymer (uncompounded and uncured), gave the following data :

300% Modulus (psi)	Tensile (psi)	Elongation (%)
340	1080	870

These runs show the great difference in properties of the block polymer as compared to a polybutadiene. The difference in properties is rendered even more unusual by the fact that inherent viscosity values were essentially the same.

Another run was made using the same recipe for the initial polymerization except that 4.67 millimoles of dilithiostilbene was used as the catalyst. After polymerizing at 50° C. for two hours, a portion (Sample B, 48.3 grams) was removed and stopped with alcohol. To the polymer solution remaining in the bottle, there was then added 25 parts of styrene. Polymerization was continued for two hours at 50° C. at which point the catalyst was inactivated with alcohol. Inherent viscosity and conversion were determined on Sample B and on the block polymer from the total polymerization. The latter was evaluated in an uncompounded and uncured state and the polystyrene content determined. Data from these determinations are shown below in Table XIII.

TABLE XIII.

	Conversion (%)	Inherent Viscosity	Modulus, (p.s.i.)	Tensile, (p.s.i.)	Elongation, (p.s.i.)	Styrene Content, Wt. %
Sample B*	100	0.58	—	—	—	—
Block polymer	102	0.65	240	410	570	21.5

* Sample B yielded a polymer which was a viscous liquid and could not be tested for modulus or tensile properties.

In this run, the inherent viscosity and physical properties reflect the higher catalyst level employed. This run is presented to demonstrate further the unusual properties of the block polymer and also to show the polystyrene content of the block polymer product.

EXAMPLE VIII.

A run was conducted in which a butadiene-styrene block polymer was prepared by charging the styrene first, followed by charging the butadiene. The following recipe was employed in this run:

	Parts by Weight Except as noted
Butadiene	70
Styrene	30
Cyclohexane	780
n-Butyllithium*	2.5 (millimoles)
Temperature, °F.	122
Total time, hours	11

* The catalyst was charged as an 0.31 M solution in an n-pentane-cyclohexane mixture which was prepared by adding cyclohexane to a 1.0 M n-butyllithium solution in n-pentane.

In this run, after charging the cyclohexane, the styrene was charged, followed by addition of the catalyst. At the end of 5 hours, the butadiene was charged, and after 6 more hours, the block polymer product was coagulated by pouring the reaction mixture into an excess of isopropyl alcohol. The conversion in this run was 96.9 per cent. The polymer product had an inherent viscosity of 0.84 (gel-free) and a refractive index at 25° C. of 1.5370.

EXAMPLE IX.

Another run was carried out in which essentially the same procedure as described in Example VIII was followed in preparing a butadiene-styrene block polymer. The following polymerization recipe was used in this run:

	Parts by Weight, Except as noted
Butadiene	70
Styrene	30
Cyclohexane	780
Tetrahydrofuran	5
n-Butyllithium*	2.5 (millimoles)
Temperature, °F.	122
Total time, hours	7

* Same as in Example VIII.

In this run, the proper amount of cyclohexane and tetrahydrofuran was charged after which the styrene and butadiene were introduced in that order. The styrene was polymerized for 5 hours while the butadiene was polymerized for 2 hours. The conversion in this run was 100 per cent, and the inherent viscosity of the polymer was 0.74 (gel-free).

The polymer of this run was then separated into fractions by solvent extraction, following the procedure described in Example II. The results of this fractionation are shown below in Table XIV.

TABLE XIV.

Fraction	Wt. % of Original	Inherent Viscosity*	Refractive Index @ 25° C.
Original	100	—	1.5318
1	38.0	0.80	1.5287
2	3.4	0.80	1.5290
3	5.5	0.81	1.5290
4	2.7	0.74	1.5288
5	3.3	0.78	1.5290
6	27.6	0.80	1.5290
7	5.25	0.79	1.5290
8	1.88	0.62	1.5291
9	10.1	0.75	1.5292
Loss	2.1		

* Gel-free.

The data in Table XIV show that the butadiene-styrene block polymer was a homogeneous polymer.

EXAMPLE X.

A series of runs was carried out in which block polymers of butadiene and styrene were prepared by initiation with 1,2-dilithio-1,2-diphenylethane, also referred to herein as dilithiostilbene. The dilithiostilbene was prepared by the reaction of trans-stilbene with lithium. Each polymerization run was carried out in a 28-ounce beverage bottle. The diluent and one of the monomers were first charged to the bottle after which the initiator was charged. The dilithiostilbene was charged as a solution in a diethyl-ether-tetrahydrofuran mixture which contained from 10 to 20 weight per cent tetra-hydrofuran. The bottle was then placed in a bath maintained at the desired polymerization temperature. After the first monomer was completely polymerized, the bottle was removed from the bath, the second monomer was charged, and the bottle was returned to the bath. When the second monomer had completely polymerized, the bottle was removed from the bath, and the polymer was coagulated by pouring the contents of the bottle into isopropyl alcohol. Before coagulation, the polymer solution was admixed with a solution of phenyl-beta-naphthyl-amine which contained an amount of this antioxidant corresponding to 2 weight per cent of the butadiene charge.

The polymerization recipes and the operating conditions used in these runs were as follows :

	Parts by Weight, Except as noted				
	A	B	C	D	E
1,3-Butadiene (Bd) ..	90	80	70	75	50
Styrene (Sty)	10	20	30	25	50
Cyclohexane ..	1170	1170	1170	585	1170
Dilithiostilbene, millimoles	*	*	*	*	*
Temperature, °F. ..	122	122	122	122	122
Charge procedure					
1st Monomer ..	Bd	Bd	Bd	Bd	Bd
Polymerization, hours	$1\frac{1}{4}$	1	1	2	$1\frac{1}{4}$
2nd Monomer ..	Sty	Sty	Sty	Sty	Sty
Polymerization, hours	2	1	$1\frac{1}{4}$	2	$1\frac{3}{4}$
Total Time, hours ..	$3\frac{1}{4}$	2	$2\frac{1}{2}$	4	$2\frac{1}{2}$
Molarity of Initiator solution	0.18	0.175	0.18	0.175	0.18

* Variable.

The results of these runs are shown herein-below in Table XV. The block polymers prepared in these runs were all of the type wherein the central block was a homo-polymer of 1,3-butadiene and the two ter-minal blocks were polystyrene. The figures in the table immediately below each of the run numbers define in weight per cent the composition of the block polymer.

TABLE XV.

Run No.	33	34	35	36	37
	5—90—5	10—80—10	15—70—15	12.5—75—12.5	25—50—25
Recipe	A	B	C	D	E
Dilithiostilbene, millimoles	1.80	3.75	3.75	2.5	6.5
Conversion, %	100	100	100	100	99
Mooney Value, ML–4	30	33.5	42	—	55
Inherent Viscosity*	1.57	0.88	0.63	0.84	0.36
Styrene Content, wt. % by ultra-violet method	10.7	20.0	32.0	21.5	50.9

* All of these polymers were gel-free.

In determining the styrene content by the ultra-violet method, the polymers are first purified to remove antioxidant by either a reprecipitation method or by extraction dis-tillation with an ethanol-toluene azeotrope. After this purification, a sample of the poly-mer on which the determination is to be made is dissolved in chloroform to form a solution containing 0.2 gram per 100 milli-liters of solution. At the same time, a sample of commercial polystyrene is dis-solved in chloroform to form a solution con-taining 0.8 gram per 100 milliliters of solu-tion. The two solutions are then scanned under ultra-violet light over the range be-tween 240 and 330 millimicrons. The actual reading point for styrene content is taken at 262 millimicrons. The amount of styrene present in the block polymer is then calcu-lated by comparing the peak height of the block polymer ultra-violet spectrum with the peak height for the polystyrene ultra-violet spectrum, using the specific extinction coefficient which was calculated for the polystyrene sample.

The polymer of run 33 was separated into fractions by solvent extraction, following the procedure described in Example II. The results of this fractionation are shown below in Table XVI.

TABLE XVI.

Sample	Wt. % of Original	Refractive Index @ 25° C.	Inherent Viscosity
Original	100	1.5225	1.57
1	24.1	1.5210	1.75
2	9.2	1.5211	1.67
3	14.5	1.5216	1.65
4	13.0	1.5217	1.52
5	17.0	1.5222	1.44
6	4.9	1.5225	1.41
7	1.5	1.5231	1.33
8	5.3	1.5249	1.15
Loss	10.5		

The data in Table XVI show that the block polymer of run 33 was a homogeneous poly-mer.

The block polymer of run 35 was tested in the unvulcanized state to determine its elastic properties. The polymer was pressed into slabs at a temperature between 220 and 260° F. after which tensile bars were cut from the slabs. These bars were then pulled on an " Instron " (Registered Trade Mark), tester at a cross-head speed of 20 inches per minute. The results of these tests are shown hereinbelow in Table XVII.

TABLE XVII.

	Run 35
Yield Stress, p.s.i. (1)	230
Approximate Elongation at yield point, per cent (1) ..	30
Maximum or Breaking Stress, p.s.i. (1)	1200
Elongation at Break, per cent (1)	76

(1) ASTM D–412–51T.

The polymer of run 35 was compounded with 0.5 part of dicumyl peroxide per 100 parts of polymer. The compounded polymer was then cured at 307° F. after which the stress-strain properties of the polymer were determined. The results of these tests are set forth hereinbelow in Table XVIII.

TABLE XVIII.

	Run 35
300% Modulus, p.s.i. (1) ..	570
Tensile Strength, p.s.i. (1) ..	1320
Elongation, per cent (1) ..	740

(1) ASTM D–412–51T.

EXAMPLE XI.

A series of runs was carried out in which block polymers having a high styrene content were prepared and then evaluated as plastics. The procedure employed in carrying out these runs was essentially the same as that described in Example X. These block polymers were also of the type wherein the central block was a homopolymer of 1,3-butadiene and the terminal blocks were polystyrene. The three numerals shown immediately below the run numbers in Table XIX hereinafter represent the weight per cent of the polymer blocks contained in the polymer composition. In carrying out the runs, the diluent was charged first after which the butadiene was added. The initiator (dilithiostilbene) was then charged, and the butadiene was polymerized to completion. The styrene was then charged, and after the styrene had all polymerized, the resulting block polymer was coagulated by discharging the reaction mixture into an excess of isopropyl alcohol. The recipe employed in these runs was as follows :

	Parts by Weight Except as noted.
Butadiene	variable
Styrene	variable
Cyclohexane	1170
Dilithiostilbene*, millimoles	0.7
Temperature, °C.	50
Time, total (hours)	4
Butadiene	2
Styrene	2

* Charged as an 0.199 M solution in a mixture of diethyl ether and tetrahydrofuran.

The results of these runs are set forth hereinbelow in Table XIX. In the runs, 1 per cent by weight, based on the butadiene content, of 4,4¹-thiobis-(6-tert-butyl-m-cresol) was admixed with the wet crumb after coagulation.

TABLE XIX.

Run No.	38	39	40	41	42
	37.5—25—37.5	40—20—40	42.5—15—42.5	45—10—45	47.5—5—47.5
Parts Butadiene by wt.	25	20	15	10	5
Parts Styrene by wt.	75	80	85	90	95
Conversion, %	98	97	97.5	100	100
Inherent Viscisity (1)	2.28	2.70	2.24	1.95	4.58
Tensile Strength, p.s.i. (2)	1633	2343	3717	5483	3693
Elongation, per cent (2)	17	33	35	2	1.9
300% Modulus, p.s.i. (3)	58,000	106,000	180,000	268,000	382,000
Izod Impact, ft. lb./in. notch (4)	14.7	1.24	0.42	0.21	0.32

(1) All of the polymers were gel-free.
(2) ASTM D-412-51T. The sample in run 42 was pulled at 0.05 inch per minute; all other samples were pulled at 0.5 inch per minute.
(3) ASTM D790-49T.
(4) ASTM D-256-56.

EXAMPLE XII.

A series of runs was carried out in which block polymers containing a central poly-butadiene block and terminal polystyrene blocks were prepared. The recipes used in these runs were as follows:

Parts by Weight, Except as noted

Run No.	43	44	45	46	47
Butadiene	90	80	70	60	50
Styrene	10	20	30	40	50
Cyclohexane	1170	1170	1170	1170	1170
Dilithiostilbene, millimoles*	2.0	2.0	2.0	2.0	2.0
Temperature, °F.	122	122	122	122	122
Time (total), hours	4	4	4	4	4

* 0.199 M in a mixture (90/10 by weight) of diethyl ether/tetrahydrofuran.

The runs were carried out by charging the cyclo-hexane, butadiene and dilithiostilbene in that order. After the butadiene had polymerized for 2 hours, the styrene was charged and allowed to polymerize for two hours. The results of these runs are shown hereinbelow in Table XX.

TABLE XX.

Run No.	Conversion, %	Refractive Index @ 25° C.	Inherent Viscosity*
43	98.5	1.5128	1.35
44	98.5	1.5285	1.18
45	99	1.5361	1.06
46	97.5	1.5430	0.94
47	96.5	1.5504	0.91

* Gel-free.

The polymers from these runs were formed into tensile bars and pulled to determine their tensile strength. The results of these tests are shown below in Table XXI.

TABLE XXI.

Run No.	Tensile Strength of Uncompounded Polymer at Test Temperature, p.s.i. (1)		
	$-1°$ C.	$25°$ C.	$60°$ C.
43	580	135	16
44	1880	560	180
45	3400	2200	1000
46	4100	2650	1370
47	5300	3900	2500

(1) ASTM D–412–51T.

From the data in Table XXI, it is seen that the tensile strength of the block polymers increased with an increase in the styrene content.

EXAMPLE XIII.

Another series of runs was carried out in which block polymers containing a central polybutadiene and terminal polystyrene blocks were prepared. In run 50 shown in Table XXII below, sufficient styrene was charged along with the butadiene to form a central block containing 10 parts of styrene for every 70 parts of butadiene. Thus, the final block polymer contained a central copolymer block comprising a 70/10 butadiene/styrene copolymer and terminal blocks of polystyrene, each containing 10 parts styrene. The recipe employed in these runs was as follows:

	Parts by Weight, Except as noted
Butadiene (Bd)	variable
Styrene (Sty)	variable
Cyclohexane	1170
Dilithiostilbene, millimoles*	variable
Temperature, °C.	50
Time	variable

* Charged as an 0.182 M solution in a mixture of diethyl ether and tetrahydrofuran except in run 50, wherein the molarity was 0.178.

In all of these runs, except as noted above for Run 50, the butadiene was charged first and allowed to polymerize after which the styrene was charged. The results of these runs are shown hereinbelow in Table XXII.

TABLE XXII.

Run No.	48	49	50
	5 Sty—90 Bd—5 Sty	15 Sty—70 Bd—15 Sty	10 Sty—(70/10 Bd/Sty)—10 Sty
Parts by Wt. Bd	90	70	70
Parts by Wt. Sty	10	30	30
Dilithiostilbene, millimoles	1.10	3.0	3.2
Polymerization Time, hours Bd	1½	1½	3
Polymerization Time, hours Sty	1½	1½	2
Conversion, per cent	100	99.5	100
Mooney Value, ML-4	76	63	72
Inherent viscosity (1)	2.03	0.69	0.87
Styrene content by U.V. (2)	10.2	—	31.3

(1) Gel-free.

(2) Determined as described in Example X.

The block polymers prepared in the above runs were compounded and cured. The compounding recipe employed was as follows :

	Parts by Weight
Polymer ..	100
Filler (1)	50
Zinc Oxide	3
Stearic Acid	2
Antioxidant (2)	1
Disproportionated Rosin	3
Sulfur	2.5
Diphenylguanidine	1.5
Benzothiazyl disulfide ..	0.75
Triethanolamine	1.0

(1) See Table XXIII for specific filler.

(2) Physical mixture containing 65 weight per cent of a complex diarylamino-ketone reaction product and 35 weight per cent of N,N¹-diphenyl-p-phenylenediamine.

The compounded stocks were cured at 307° F. for 45 minutes and the physical properties determined. The results of these runs are shown hereinbelow in Table XXIII.

TABLE XXIII.

Run No.	48		49		50	
Mooney Viscosity, ML-4	76		63		72	
Filler, phr	50 (1)	50 (2)	50 (1)	50 (2)	50 (1)	50 (2)
$v \times 10^4$ (3)	2.00	2.50	1.00	1.35	1.15	1.15
300% Modulus, p.s.i. (4)	730	900	1480	1610	1340	1330
Tensile, p.s.i. (4)	970	1180	1950	1990	2140	1960
Elongation, per cent (4)	400	410	410	390	470	460
Resilience, per cent (5)	77.0	72.0	51.0	49.3	58.0	68.7
Hysteresis, T, °F. (5)	47.3	57.5	165.3	149.1	112.9	149.0

(1) Hard-type, white to cream-colored kaolin mineral filler (aluminium silicate) sold by R. T. Vanderbilt Co. as Dixie Clay.
(2) Hydrated Silica.
(3) See Footnote (4), Table XII of Example VI.
(4) ASTM D412–51T.
(5) ASTM D632–55T.

EXAMPLE XIV.

A series of runs was carried out in which block polymers were prepared and evaluated. The polymerization recipes and the operating conditions used in these runs are as follows :

	Parts by Weight, Except as Noted	
	A	B
Butadiene (Bd)	70	70
Styrene (Sty)	30	30
Cyclohexane	1170	1170
Tetrahydrofuran	1.4	1.4
Dilithiostilbene, millimoles*	3.25	3.25
Temperature, °F.	122	122
Time (total), hours	5	5
First Polymerization Charge, Butadiene	70	68
Time, hours	3	3
Second Polymerization Charge	30 Sty	2 Bd /30 Sty
Time, hours	2	2

* Charged as 0.218 M solution in mixture of diethyl ether and tetrahydrofuran.

The results of these runs are shown herebelow in Table XXIV.

TABLE XXIV.

Run No.	51	52
	15 /70 /15 Sty—Bd—Sty	1 /15—68—1 /15 Bd /St—Bd—Bd /Sty
Block Polymer, Composition Recipe	A	B
Mooney Viscosity, ML-4	48	28
Inherent Viscosity*	0.93	0.76
Refractive Index at 25° C.	1.5360	1.5366
Molecular Weight**	31,000	31,000

* All polymers were gel-free.
** Estimated from initiator level.

From the data in Table XXIV, it is seen that a large change in the ML–4 value resulted from forming the terminal blocks by copolymerizing a small amount of butadiene with the styrene.

The tensile properties of the block polymers of runs 51 and 52 were determined on the uncured and uncompounded stocks. These properties are shown hereinbelow in Table XXV.

TABLE XXV.

Run No.	51	52
300% Modulus, p.s.i. (1)	330	290
Tensile Strength, p.s.i. (1)	760	670
Elongation, per cent (1)	690	730
Elastic Recovery, per cent	97.8	97.8

(1) ASTM D412–51T.

EXAMPLE XV.

Several runs were carried out in which block polymers of butylene and styrene were prepared. These block polymers contained a central block of polystyrene amounting to 75 parts per 100 parts of the polymer and terminal blocks of polybutadiene each containing 12.5 parts per 100 parts of polymer. These runs were carried out in accordance with the following recipes.

Parts by Weight, except as noted

	A	B
Butadiene (Bd)	25	10
Styrene (Sty)	75	90
Cyclohexane	1170	1170
Dilithiostilbene, millimoles*	variable	variable
Temperature, °C.	122	122
Time (total), hours	6	6

* Charged as an 0.218 M solution in a mixture of diethyl ether and tetrahydrofuran.

In these runs, the styrene was charged first and polymerized for three hours, after which the butadiene was charged and polymerized for three hours. The results of these runs are shown hereinbelow in Table XXVI. Physical properties of the polymers are also included in this table.

TABLE XXVI.

Run No.	56	54	55	56
Recipe	A	A	B	B
Dilithiostilbene, millimoles	0.9	0.6	0.9	0.6
Conversion, per cent	99.5	96.5	96.7	96.5
Inherent Viscosity (1)	1.55	2.80	1.42	2.34
Physical Properties :				
Tensile Strength, p.s.i. (2)	3113	2940	5113	4800
Elongation, per cent (2)	3	3	3	4
300% Modulus, p.s.i. (3)	253,000	263,000	337,000	387,000
Impact Strength, ft. lb. /inch				
Notch (4)	0.76	1.16	0.40	0.46

(1) Gel-free.
(2) ASTM D412–51T.
(3) ASTM D790–49T.
(4) ASTM D256–56.

EXAMPLE XVI.

A series of runs was carried out in which butadiene-styrene block polymers of high styrene content were prepared. In these runs, the diluent and butadiene were charged first after which the initiator was added. After a 6-hour polymerization period, the styrene was added. At the end of the pol,merization, the polymer was coagulated by dumping the polymerization mixture into an excess of isopropyl alcohol. The polymerization recipes employed in these runs were as follows:

			Parts by Weight, except as noted			
			A	B	C	D
Butadiene (Bd)	..	..	25	25	10	25
Styrene (Sty)	..	..	75	75	90	75
Cyclohexane ..	..	..	1170	780	780	780
Tetrahydrofuran	..	..	2	0	0	0
n-Butyllithium, millimoles	..		variable	variable	variable	variable
Temperature, °F.	..	..	122	122	122	122
Total time, hours	..	..	24	8	8	21
Styrene Time, hours		..	18	2	2	15
Butadiene Time, hours		..	6	6	6	6

The results of these runs are shown hereinbelow in Table XXVII. This table also includes physical properties of the block polymers.

TABLE XXVII.

Run No.	57	58	59	60
Recipe	A	B	C	D
n-Butyllithium, millimoles	2.1	1.8	1.8	1.1
Conversion, per cent ..	100	100	98.2	98.5
Inherent Viscosity (1) ..	0.73	0.72	0.66	1.77
Physical Properties:				
Tensile Strength, p.s.i. (2)	1,860	1,478	2,723	1,550
Elongation, per cent (2) ..	1	1	1.5	1
300% Modulus, p.s.i. (3)	243,000	238,000	319,000	231,000
Impact Strength (4)				
ft. lb./inch notch ..	0.26	0.30	0.32	0.61

(1) Gel-free.

(2) ASTM D412–51T.

(3) ASTM D790–49T.

(4) ASTM D256–56.

In the above runs, the wet crumb which was obtained from the alcohol coagulation was mixed with a solution of 4,4¹-thiobis-(6-tert-butyl-m-cresol) in isopropyl alcohol to provide an antioxidant concentration in the polymer of 1 weight per cent, based on the butadiene. The samples were then vacuum dried at 57° C. for 24 hours, after which they were cut into small pieces and dried under vacuum at 57° C. for an additional 18 hours.

EXAMPLE XVII.

A series of runs were carried out in which block polymers of butadiene and 2-vinyl-pyridine were prepared. The recipe for this run was as follows:

	Parts by Weight except as noted
Butadiene (Bd)	variable
2-Vinylpyridine (VP)	variable
Cyclohexane	1060
Dilithiostilbene, millimoles	20
Temperature, °C.	50
Time (total), hours	2
Butadiene polymerization time, hours	1
Vinylpyridine polymerization time, hours	1

In these runs, the butadiene was charged initially after which the 2-vinylpyridine was charged as a 10 per cent by weight solution in cyclohexane. The results of these runs are expressed as Table XXVIII.

TABLE XXVIII.

Run No.	61	62	63	64
Parts Butadiene	90	95	98.5	99
Parts Vinylpyridine	10	5	1.5	1.0
Conversion, per cent	100	100	100	100
Appearance	solid	solid	sticky but firm	

EXAMPLE XVIII.

A series of runs were carried out in which block polymers of butadiene and acrylonitrile were prepared. The recipes for these runs were as follows :

	Parts by Weight, except as noted	
Run No.	65	66
Butadiene (Bd)	90	70
Acrylonitrile (Ac)	10	30
Cyclohexane	780	780
Dilithiostilbene, millimoles*	5.0	5.0
Temperature, °C.	30	30
Nitrogen purge (3 l./min.), min./ml.	0.083	0.083
Bd Polymerization time, hours	6	6
Ac Polymerization time, hours	21	21

* Charged as 0.256 M solution in a mixture of diethyl ether and tetrahydrofuran.

In these runs, the diluent was charged initially followed by the butadiene and catalyst. After a period of 6 hours, the acrylonitrile was charged. A firm gel formed almost immediately when the acrylonitrile was added. The per cent conversions obtained on runs 65 and 66 were 100 and 97, respectively.

The block polymers produced in accordance with this invention can be rubbery or plastic materials. In general, the polymers have utility in application where plastic polymers and natural and synthetic rubbers are used. The polymers can be compounded by any of the known methods as have been used in the past for compounding rubbers and plastics. Compounding ingredients, such as fillers, dyes, pigments, curing or cross-linking agents, softeners, reinforcing agents and the like, can be used in the compounding operation. In manufacturing finished articles, the block polymers can be molded or extruded. They can be advantageously employed in the manufacture of items such as automobile tires, gaskets, containers, pipe, and the like.

From the foregoing, it is seen that a variety of block polymer products can be prepared in accordance with this invention. Thus, the process of this invention makes it possible to obtain a product ranging, e.g., from rubbery to plastic materials, and having a desired set of physical properties. While the block polymers preferably contain either two or three polymer blocks or segments, it is within the scope of the invention to prepare polymers having any number of polymer blocks. The amount of a particular monomer in a particular homopolymer block, or in the case of a copolymer block, the amount

of the monomers forming the particular copolymer block is preferably at least 5 weight per cent of the total weight of the block polymer molecule. It is to be understood that block polymers prepared in accordance with this invention contain the hydrocarbon radical of the organolithium compound used in the polymerization. For example, when a compound such as butyllithium is employed, the butyl radical is located at one end of the block polymer molecule. In a polymerization using dilithiostilbene as the catalyst, the diphenylethylene radical is incorporated in the polymer block which is initially formed.

We are now aware of Specifications 856,581 and 852,823 which were not published at the application date of the present application but which bear earlier respective dates.

WHAT WE CLAIM IS :—

1. A process for preparing block polymers from monomers selected from (1) 1,3-butadiene, 2-methyl-1,3-butadiene, 1,3-pentadiene and vinyl-substituted aromatic hydrocarbons, (2) vinylpyridines and (3) vinyl halides, vinylidene halides, acrylonitrile, esters of acrylic acid and esters of homologues of acrylic acid, which comprises initially contacting a first monomer selected from the monomers in said groups (1) and (2) with a catalyst corresponding to the formula $R(Li)_x$, wherein R is a hydrocarbon radical selected from aliphatic, cycloaliphatic and aromatic radicals and x is an integer from 1 to 4, inclusive, in the presence of a hydrocarbon diluent selected from aromatic, paraffinic and cycloparaffinic hydrocarbons so as to form a polymer block of said selected monomer ; and, after polymerization of substantially all of said selected first monomer, contacting said catalyst in the presence of said polymer block and said hydrocarbon diluent (A) with a second monomer selected from the monomers in said groups (1), (2) and (3) when said first monomer is a monomer of group (1) or (B) with a second monomer selected from the monomers in said group (3) when said first monomer is a monomer of group (2), said second monomer being different from the monomer employed in said initial contacting.

2. A process according to Claim 1, wherein said initial and subsequent contacting steps are carried out at a temperature of from −80 to 150° C. and preferably at a temperature of from − 20 to 80° C. and at a pressure sufficient to maintain the reaction mixture substantially in the liquid phase.

3. A process according to Claim 1 or 2, wherein said first monomer is 1,3-butadiene and said second monomer is styrene, acrylonitrile, or 2-vinylpyridine.

4. A process according to Claim 1 or 2, wherein said first monomer is styrene and said second monomer is 1,3-butadiene or 2-vinylpyridine.

5. A process according to Claim 1 or 2, wherein said first monomer is 2-methyl-1,3-butadiene.

6. A process according to any one of the preceding claims, wherein said catalyst is n-butyllithium, isopropyllithium, phenyllithium, n-decyllithium, cyclohexyllithium or 1,2-dilithio-1,2-diphenylethylene.

7. A process according to any one of the preceding claims, wherein said hydrocarbon diluent has in admixture therewith from 0.005 to 50 weight per cent, based upon the total mixture, of a polar organic compound.

8. A process according to Claim 1, wherein one of said conjugated dienes is initially contacted with said catalyst in the presence of said hydrocarbon diluent and a polar organic compound, said polar compound being present in an amount of from 0.005 to 50 weight per cent based upon the total mixture, allowing a portion of said conjugated diene preferably 25 per cent thereof to polymerize and then adding said second monomer to the reaction zone, recovering from said zone a block polymer comprising a homopolymer block of said conjugated diene and a copolymer block of said conjugated diene and second monomer.

9. A process according to Claim 1, wherein one of said conjugated dienes and a vinyl-substituted aromatic hydrocarbon are added to the reaction zone and initially contacted with said catalyst in the presence of said hydrocarbon diluent and a polar organic compound, said polar compound being present in an amount of from 0.005 to 50 weight per cent based upon the total mixture, allowing the polymerization to proceed to substantially 100 per cent conversion and then adding a conjugated diene to said reaction zone, recovering from said zone a block polymer comprising a copolymer block and a homopolymer block.

10. A process for preparing block polymers substantially as hereinbefore described with reference to the examples.

11. A block polymer of substantially uniform molecular weight prepared in the presence of a lithium-containing catalyst, which comprises at least two polymeric blocks linked to one another, one of said polymeric block being formed by the polymerization of at least one monomer selected from 1,3-butadiene, 2-methyl-1,3-butadiene, 1,3-pentadiene, vinyl-substituted aromatic hydrocarbons, and vinylpyridines containing a vinyl radical as the sole substituent, and another of said polymeric blocks being formed by the polymerization of at least one monomer selected from 1,3-butadiene, 2-methyl-1,3-butadiene, 1,3-pentadiene, vinyl-

substituted aromatic hydrocarbons, vinyl-pyridines containing a vinyl radical as the sole substituent, vinyl halides, vinylidene halides, acrylonitrile, esters of acrylic acid and esters of homologues of acrylic acid, said polymeric block formed by the polymerization of vinyl-pyridines being linked only to a polymeric block formed by the polymerization of at least one monomer selected from vinyl halides, vinylidene halides, acrylonitrile, esters of acrylic acid and esters of homologues of acrylic acid, and at least one monomer used in forming said first-mentioned polymeric block being different from at least one monomer used in forming said second-mentioned polymeric block.

12. A block polymer according to Claim 11, comprising a central polymer block of 1,3-butadiene and terminal polymer blocks of styrene, acrylonitrile or 2-vinylpyridine.

13. A block polymer according to Claim 11, comprising a central polymer block of styrene and terminal polymer blocks of 1,3-butadiene.

14. A block polymer according to Claim 11, comprising a polymer block of 1,3-butadiene and a polymer block of styrene.

15. A block polymer substantially as hereinbefore described with reference to the examples.

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